

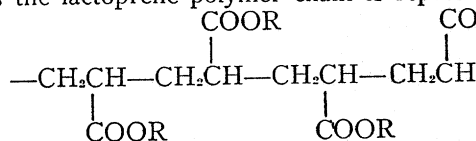
Lactoprene EV Elastomer Curing Recipes and Properties

LACTOPRENE is the name of a new type of synthetic rubber, based on acrylic esters, which can be made from various raw materials, such as milk, sugar, starch, molasses, and wood, as well as from petroleum and coal. Lactoprene is highly superior to natural rubber in some respects, but inferior in others. It has special properties that make it useful for some purposes for which natural rubber and some synthetic rubbers are clearly unsatisfactory. Lactoprene should be particularly valuable for uses that require excellent flex life and resistance to oxidation, oils, and aging at either normal or elevated temperatures.

Polymerization, the process employed for the preparation of various other synthetic rubbers, is used to make lactoprene. Unlike many of the synthetic rubbers, lactoprene is not a butadiene or diene copolymer; it is a copolymer made with an acrylic ester, such as ethyl acrylate, as the principal monomer. Although butadiene rubbers and acrylic elastomers are structurally similar in having a long carbon chain, the butadiene chain has olefinic linkages and no ester groups; whereas the acrylic chain has ester groups, but no olefinic linkages. A portion of a butadiene polymer chain may be written as



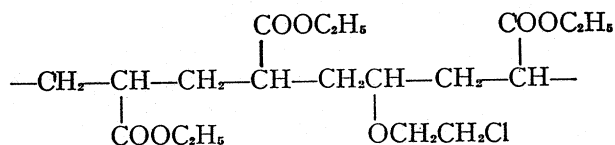
whereas the lactoprene polymer chain is represented as



These structural features have a direct bearing on the properties of the raw polymer and the vulcanizates. The olefinic linkages, needed for the vulcanization of butadiene polymers and natural rubber, facilitate oxidation and are largely responsible for deterioration and aging. Not having olefinic linkages, lactoprene is resistant to oxidation and weathering. New methods which eliminate the need of olefinic linkages are used to vulcanize lactoprene. The oxygen-containing ester groups in lactoprene are probably responsible for its oil resistance.

Various types of acrylic elastomers have been made by polymerizing different acrylic esters, $\text{CH}_2:\text{CHCOOR}$. Ethyl acrylate has been used in most instances, however, and most attention has been given to copolymers made by polymerizing ethyl acrylate with a small quantity of a halogen-containing monomer such as 3-chloropropyl acrylate ($\text{CH}_2:\text{CHCOOCH}_2\text{CH}_2\text{CH}_2\text{Cl}$) or 2-chloroethyl vinyl ether ($\text{ClCH}_2\text{CH}_2\text{OCH}:\text{CH}_2$). Lactoprene EV is made by polymerizing an emulsified mixture of 95% ethyl acrylate and 5% chloroethyl vinyl ether. Although it cures somewhat more slowly than the corresponding ethyl acrylate-chloropropyl acrylate copolymer (1),² it is generally similar in other respects. Lactoprene EV presumably has the following chain structure.

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Special Properties and Advantages of Lactoprene

In describing the properties and potential uses of lactoprene, it is compared with standard GR-S, now produced in large quantities as a large-volume general-purpose synthetic rubber. Based on such a comparison, the advantages and disadvantages of lactoprene are summarized as follows:

COMPARISON OF LACTOPRENE EV WITH STANDARD GR-S RUBBER
Highly superior or advantageous to GR-S with respect to:

1. Flex life (2)
2. Oil resistance (3)
3. Resistance to oxidation and aging at normal and elevated temperatures (3)
4. Resistance to sunlight

Superior or advantageous with respect to:

1. Permeability to hydrogen, helium, and carbon dioxide³
2. Retention of elongation at high temperature⁴
3. Abrasion resistance (according to limited available data).
4. Ease and simplicity of production
5. Yield from carbohydrate sources
6. Suitability for production of white stocks or articles having pastel shades

Equal with respect to:

1. Ease of pigment incorporation⁴
2. Variety of curing recipes and rate of curing
3. Retention of tensile strength at 212° F.⁴
4. Permanent set⁴
5. Resilience at 212° F.⁴

Inferior with respect to:

1. Tensile strength at normal temperatures (slight when compared with similarly loaded GR-S)⁴
2. Retention of modulus at 212° F. except in the longer cures⁴
3. Compression set (slight)
4. Heat build-up (except for higher cures)⁴
5. Resilience at room temperature⁴
6. Flexibility at low temperatures (but sufficiently flexible—if plasticized—at temperatures normal in civilian applications)
7. Resistance to steam
8. Swelling in water (although undesirable for some applications, this characteristic might be advantageous for the manufacture of rubber sheets, shoes, garments, etc.)
9. Cost (acrylic esters are made on a relatively small scale, but it is confidently expected that the price of acrylic esters will be substantially lowered)

The monomers used in preparing lactoprene are liquids at room temperature; hence pressure equipment is not required for polymerization or storage. The reaction progresses orderly so that polymerization regulators or measures to prevent premature cross-linkage are not required. Neither is it necessary to "short-stop" the polymerization; the reaction is carried to completion in a short time (approximately one hour), and the yield

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² Bibliography references appear at end of article.

³ Permeability data kindly supplied by L. A. Wood and T. P. Sager, of the National Bureau of Standards.

⁴ From reports entitled, "Lactoprene E170" and "Lactoprene EV-II," by Harold M. Leeper, and Technical Report SP-T-24 by E. G. Labbe and J. W. Schade, of the Government Evaluation Laboratories, Akron, O.; Lactoprene E170, a copolymer of 90% ethyl acrylate and 10% 3-chloropropyl acrylate, is similar to Lactoprene EV.

of polymer is almost quantitative. Properties may be varied over a wide range by using various acrylic esters or by copolymerizing with other monomers. The crude polymer is soluble in many organic solvents, and therefore it is suitable for the preparation of coatings and adhesives. At least two separate curing mechanisms appear to be available for vulcanization, depending on the formulation employed; hence vulcanizates having various properties can be made through the proper selection of recipe; white vulcanizates in particular and products having pastel shades are possible. Since no initial breakdown is required, the polymer is well suited to compounding in a Banbury mixer. Plasticizers and softeners are not required for compounding although they may be used successfully if desired. Acrylic esters, the monomers, can be made from petroleum, coal, or carbohydrates. One pound of carbohydrate yields approximately one pound of reinforced lactoprene vulcanizate.

POTENTIAL USES. Lactoprene naturally should prove most useful in fields in which its special properties are used to the maximum. Because of its excellent flex life, cut-growth resistance and resistance to oils, oxidation, and deterioration at normal and elevated temperatures, lactoprene should be useful, possibly preferable to other elastomers, for products such as hose, gaskets, and packings, transmission and conveyor belts, boots, soles, and heels which come in contact with oil or heat, tank linings where oil or high temperatures are encountered, printing rolls, white articles or articles having pastel shades, oil-resistant gloves and fabrics, machine and instrument supports, grommets, mats, and pads, protective covers, cements, gasoline hose nozzles, coated cloth and paper (applied from solution or water emulsion), and laminated paper and cloth.

Lactoprene has been experimentally used as latex and as rubber cement. Hard rubber-like materials have been made from lactoprene. More data are needed, however, to assess the merit and possibilities of lactoprene in these fields.

VULCANIZATION OF SATURATED POLYMERS. Rubber and most of the synthetic elastomers (4) are made vulcanizable (5) by the presence of olefinic linkages. The earliest type of lactoprene (6) was unsaturated also and, like natural rubber, was vulcanized through the olefinic linkages. A more recent type of lactoprene (1-3), however, is saturated and contains halogen, which is the active group that facilitates vulcanization. This new method of vulcanizing is versatile and has certain advantages not possessed by conventional methods. Both sulfur and various non-sulfur recipes can be used to vulcanize these lactoprene copolymers, which are essentially halogen-containing acrylic resins having rubber-like properties.

PREVIOUS WORK ON VULCANIZATION OF ACRYLIC RESINS. The first patents obtained by Rohm (7), who pioneered the industrial exploitation of acrylic resins, were concerned with making artificial rubber. Rohm prepared his rubber substitute by mixing a polymerized acrylic ester with sulfur and heating the mixture at about 40° C. for two hours. The mechanism and nature of this purported vulcanization of essentially saturated acrylic polymers were not described.

Rohm and Bauer (8) described the preparation of acrylic resin mixtures, containing mineral fillers and other materials, which they claimed were suitable for the manufacture of skidproof tires. According to the reports of other investigators (9), rubber-like materials have been made by the emulsion polymerization of acrylic esters, and the rubber-like properties of acrylic resins have been enhanced by the admixture of tannic acid,

ferric acetate, copper powder, and antimony potassium tartrate (10).

Nowak (11) claimed that vulcanization does not occur when polyacrylic esters and sulfur mixtures are heated unless a surface catalyst, such as carbon black, is present. His process of making rubber-like materials consisted in incorporating sulfur, β -naphthol, carbon black, and talc into polymerized ethyl acrylate by milling at 90 to 110° C.

Vulcanization of acrylic polymers having olefinic unsaturation has been mentioned briefly. Mark and Fikentscher (12) prepared a polymer of allyl acrylate by treating polyacrylyl chloride with allyl alcohol and stated that vulcanization transformed it into rubber-like products. The copolymers of vinyl β -methylcrotonate and an acrylic ester have been vulcanized with sulfur, presumably by unsaturation furnished by the vinyl β -methylcrotonate (13).

Butadiene and related dienes have been copolymerized with either acrylic esters (14) or methacrylic esters (15) to form rubber-like products. Usually three parts of butadiene are used for each part of acrylic ester. The resulting copolymers would be expected to have considerable unsaturation and be capable of vulcanization. Regardless of the merit of this type of synthetic rubber, such products contain more butadiene than acrylic ester and therefore are more appropriately classified as butadiene rubbers.

To the best of our knowledge the vulcanization of saturated halogen-containing acrylic resins had not been described in technical literature prior to work on lactoprene (1).

Lactoprene Raw Materials

Acrylic esters (16) ($\text{CH}_2\text{:CHCOOR}$) are the principal raw materials in the production of lactoprene copolymers, which are subsequently vulcanized to give lactoprene rubber. Ethyl acrylate ($\text{CH}_2\text{:CHCOOCH}_2\text{CH}_3$) is particularly suitable because its polymers are soft and rubbery. Polymers of methyl acrylate ($\text{CH}_2\text{:CHCOOCH}_3$) are stronger but less elastic than the polymers of ethyl acrylate. Some of the higher acrylic esters (17), such as n-butyl acrylate, yield softer and more rubbery polymers than ethyl acrylate.

Acrylic esters can be made commercially from petroleum, coal, and fermentable carbohydrates (18), such as milk sugar, corn sugar, molasses, and wood hydrolyzates, as outlined below.

Petroleum or coal)	→ ethylene	→ ethylene oxide
)	→ ethylene cyanohydrin	→ acrylic esters.
Sugar	→ lactic acid	→ methyl lactate	
	→ methyl acetyl lactate	→ methyl acrylate	
		→ higher alkyl acrylates	

A recent report (19) describes a new and inexpensive method of making acrylic acid and ethyl acrylate that was developed in Germany during World War II. The method comprises interaction of either: acetylene, water, and carbon monoxide; or acetylene, ethanol, and carbon monoxide in the presence of nickel carbonyl.

The simple acrylic polymers, such as are obtained by polymerizing ethyl acrylate, can be vulcanized with benzoyl peroxide or quinone dioxime recipes (1), but vulcanization is facilitated by the presence of halogen in the polymer. This halogen can be introduced conveniently by copolymerizing the ethyl acrylate with a small proportion (approximately 5%) of halogen-containing monomers, such as chloropropyl acrylate ($\text{CH}_2\text{:CHCOOCH}_2\text{CH}_2\text{CH}_2\text{Cl}$) or chloroethyl vinyl ether ($\text{CH}_2\text{:CHOCH}_2\text{CH}_2\text{Cl}$).

The chloropropyl acrylate has been made on a large laboratory scale by the interaction of 3-chloropropanol and methyl acrylate. Largely because of the present cost and scarcity of chloropropyl acrylate, chloroethyl vinyl ether is now preferred for the preparation of halogen-containing acrylic elastomers.

Chloroethyl vinyl ether (20) has been made by the reaction of alkali with chloroethyl ether ($\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$). The reagents needed for this preparation are now produced commercially at low cost.

The other materials (water, ammonium persulfate, emulsifiers such as Tergitol No. 4⁵ and Triton 720, and inorganic salts for coagulating the emulsion) needed for the preparation of lactoprene by emulsion polymerization (21) are readily available at low cost.

Properties of Lactoprene Copolymer

After the copolymer is washed and dried, it is a white (essentially colorless), soft, elastic solid. When obtained by coagulating an emulsion that has been thoroughly steam-distilled, the polymer is virtually odorless. The density of the polymer is approximately 1.15. Although it is insoluble in water, it swells considerably when immersed for extended periods in water. The polymer is soluble in many organic solvents, such as toluene, acetone, ethyl acetate, and dioxane. However, unless a suitably balanced solvent mixture is used, the solution is likely to exhibit considerable "false body."

In its crude form the polymer is thermoplastic, but its behavior on the mill gives the impression that it contains a large gel fraction. This indication is erroneous, however, because the polymer may be dissolved completely in a suitable solvent. Furthermore, when processing temperatures are raised, the roughness of the milled sheet, which is usually observed at ordinary milling temperatures, disappears, and the stock processes smoothly. Milling is further facilitated by one part to two parts of a processing aid such as stearic acid or a plasticizer in the compounding formula. This processing behavior is explainable if one considers the large number of polar side groups attached to the polymer chain. The existence of attractive forces between these polar groups suggests that this may be responsible for the apparent gelled character of the crude polymer.

The crude polymer does not require a preliminary breakdown on the mill. Improved tensile properties are obtained when the stock is milled on hot rolls. When Lactoprene EV is properly formulated, the compound

can be made to adhere to the front roll throughout the milling. However, unless a processing aid is added, the required milling temperature usually makes the stock too hot to handle during milling.

An important advantage of using plasticizers is that they lower the brittle point. Normally an unplasticized Lactoprene EV vulcanizate will have a brittle point in the neighborhood of -15°C . The use of 10 to 20 parts of plasticizer per 100 parts of polymer lowers the brittle point to -40°C ., as measured by the method of Selker, Winspear, and Kemp (22). Data on Plasticizer SC (23) and dioctyl sebacate as compounding ingredients are shown in Table 1, and more recent results indicate that "Thiokol" TP90-B, Flexol 4GO, and other plasticizers may be used to advantage.

VULCANIZATION AND CURING RECIPES. Lactoprene EV copolymer contains the active chlorine center for vulcanization in addition to the functional groups present in polyethyl acrylate. Thus it is vulcanizable not only with the agents capable of curing polyethyl acrylate [(a) the hydroxides of certain bivalent metals (24), (b) the oxides of these bivalent metals used with stearic acid, (c) quinone dioxime and certain metal oxides, and (d) benzoyl peroxide], but also with numerous other agents, including sulfur, sulfur-bearing compounds, amines, and Polyac (25). Moreover, in some instances when agents capable of curing polyethyl acrylate are used with Lactoprene EV, the curing rate is higher, and better physical properties are obtained.

From these observations one concludes that copolymerizing with chloroethyl vinyl ether further facilitates vulcanization of the acrylic elastomer.

Lactoprene EV usually cures more slowly than the general-purpose synthetics when the comparison is based on a common recipe. The acrylic copolymer stock differs from the diene synthetics (26) in that it has a so-called optimum cure, and reversion of tensile properties occurs with overcure. However, under ordinary conditions, optimum modulus is usually obtained in anywhere from six to 72 hours at 300°F ., depending upon the compounding formula employed. The fast-curing amine recipes usually produce vulcanizates which revert rapidly, as indicated by change in tensile properties during prolonged exposure to dry heat (2, 3). Conversely, vulcanizates formulated by slow-curing sulphur recipes exhibit extended resistance to heat. Thus the combination of a fast- and a slow-curing agent in the compounding recipe may be expected to yield a vulcanizate having the best combination of rapid vulcanization and heat resistance.

⁵ The mention of this product and other commercial products does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.

TABLE 1. VULCANIZATION OF LACTOPRENE EV WITH SULFUR AND POLYAC RECIPES*

Recipe No.	2097†	2094	2111	2109	2096	2159†	2160†	2084†	2075	2106†	2082†	2099
Sulfur	1	1	2	2	1	2	2					
Tuads				1				2	1			
Monex		2	1									8
Litharge	8										2	
Accelerator 808	3				2							
Stearic acid			2									
Rotax				0.5								
Pipsolene						1	1					
Plasticizer SC						10						
Dioctyl sebacate							10					
Polyac								4	2	3	3	3
Triethylene tetramine												
Trimene base										2		
Cure, min. at 312°F . ..	30	60	120	120	30	120	120	120	120	30	120	120
Tensile strength, p.s.i. ...	1330	1280	1290	1230	1050	1670	1800	1420	1570	1310	1410	1490
Elongation, %	470	770	640	650	390	510	450	590	440	360	520	340
Shore A hardness	55	41	49	45	44	53	51	54	50	54	55	54
Crescent tear, lb./in. ...	174	106	133	90	97	280	320	197	79	160	175	174
Resilience, %	2	2	2	1	2	6	4	2	2	2	3	3
Break set	10	15	18	13	10	26	23	21	7	8	8	10
Oven aged at 300°F . for 3 days:												
Tensile, p.s.i.	1810	920	380	1080	1020	1840	1540	1350	1340	1920	1388	1960
Elongation, %	110	490	560	430	160	340	280	320	260	60	160	70
Hardness, Shore	81	39	42	46	56	64	70	70	62	87	74	85

*100 parts Lactoprene EV and 30 parts SRF carbon black used in each recipe.
†50 parts SRF carbon black.

Although many recipes may be used for vulcanizing lactoprene, the following has been used most frequently in recent work:

Ingredient	Parts
Copolymer	100
SRF black	50
Stearic acid	1
Monex	1
Trimene Base	1
Sulfur	2
	155

Compounding and curing Lactoprene EV with this recipe has been described in detail elsewhere (3). It is principally designed for producing vulcanizates of superior heat resistance. Stocks compounded according to this recipe cure at a reasonable rate, and the resulting vulcanizate has unusual resistance to aging by dry heat, even at temperatures as high as 300° F. However the recipe has not been critically evaluated. The Trimene Base is introduced to insure comparatively rapid curing; whereas the sulfur and Monex are responsible for a delayed cure; the combination produces a stock of broad curing range. For practical reasons it has been customary to cure this stock for one hour to two hours at 298° F. The result is a somewhat undercured vulcanizate, as indicated by the increase in modulus during heat aging at 300° F. For more rapid curing it would probably be advantageous to increase the proportion of amine and possibly compensate by reducing the amount of sulfur. It must be remembered that the observations on the delayed curing characteristics are based on heat-aging data (air cure). Under these conditions a portion of the free vulcanizing agents in the cured specimen may be fugitive. This view is supported by the fact that the tensile properties of specimens of this vulcanizate which are aged in a circulating-air oven tend to revert whereas similar specimens aged in Wood's metal at the same temperature continue to harden. Thus

in adjusting the recipe the conditions of exposure must be kept in mind if stability of the vulcanizate is to be maintained.

Numerous curing recipes for lactoprene have been used, and the results shown in Tables 1, 2, and 3 demonstrate that various types of agent can be used to vulcanize halogen-containing acrylic elastomers. The tensile properties exhibited, however, are in most cases suggestive of relative rates of cure only. It must be remembered that these stocks are with few exceptions slow to reach optimum cure so that they may be expected to be undercured to varying degrees, dependent upon the relative efficiencies of the curing agents used.

TABLE 2. VULCANIZATION OF LACTOPRENE EV*

Recipe No.	2073	2141	2074	2064	2104	2076
Sulfur	2	2				
Monex	1					
Tuads			2			
Pipsolene		1				
Polyac			3			
Triethylene tetra- mine					1	0.5
p-Quinone dio- xime (G.M.F.)				2		
Accelerator 808					3	
Stearic acid				3		
Litharge					8	
Red lead				10		
Zinc oxide				10		
Curing time, min.	60	120	60	120	120	60
Cure temp., °F.	312	312	312	312	298	298
Tensile strength, p.s.i.	1530	1650	1500	1460	1740	1100
Elongation, %	710	610	490	420	670	570
Shore A hard- ness	41	45	47	50	45	50
Crescent tear, lb./in.	102	87	172	145	96	199
Break set, %	18	18	10	10	17	18
Resilience, %	2	3	2	3	3	4
Oven aged 3 days at 300° F.						
Tensile, p.s.i.	1730	1360	1300	3910	2280	630
Elongation, %	440	420	410	30	60	100
Hardness, Shore	50	49	50	100	92	62

*All recipes contained 100 parts Lactoprene EV and 30 parts SRF black.

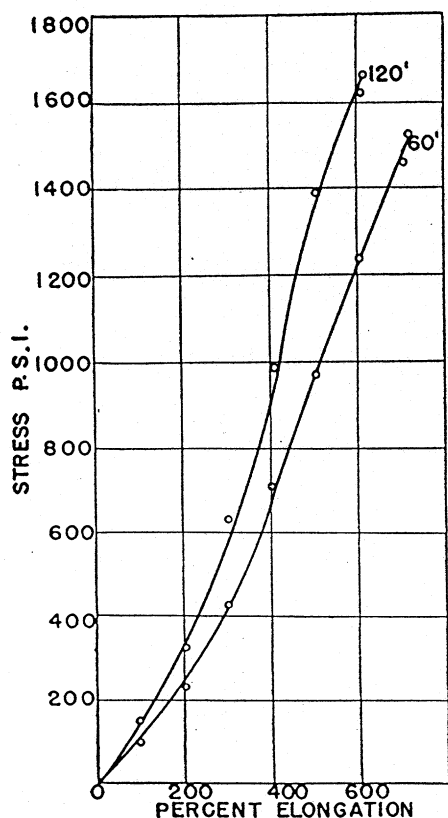


Fig. 1. Stress-Strain Curves of Lactoprene EV Cured with Sulfur and Monex (2073)

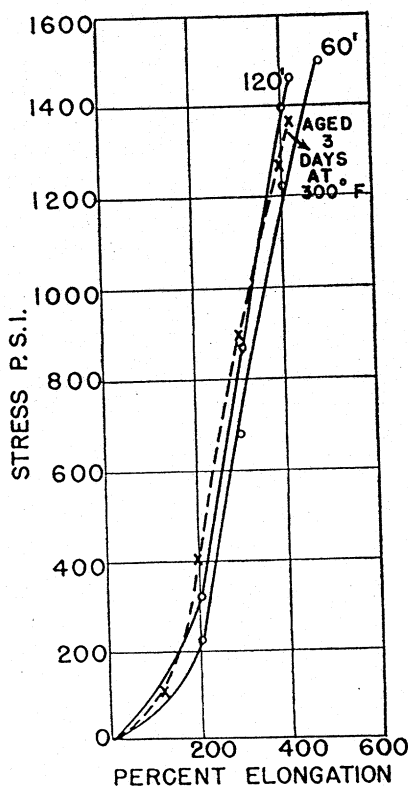


Fig. 2. Stress-Strain Curves of Lactoprene EV Cured with Sulfur and Pipsolene (2141)

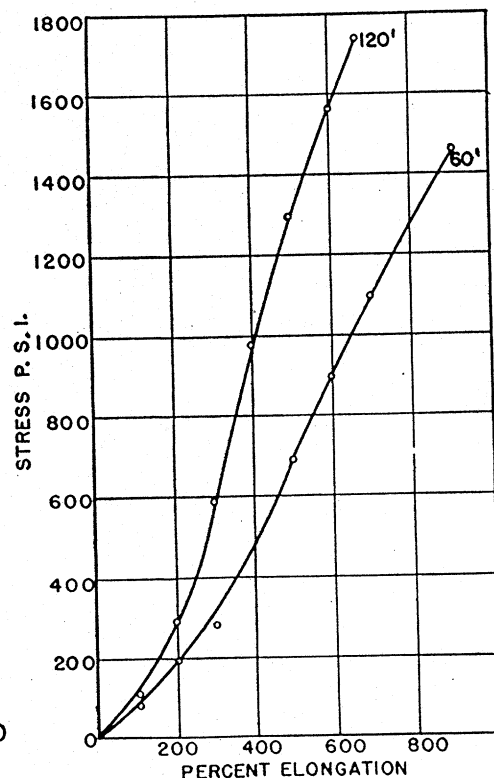


Fig. 3. Stress-Strain Curves of Lactoprene EV Cured with Polyac and Tuads (2074)

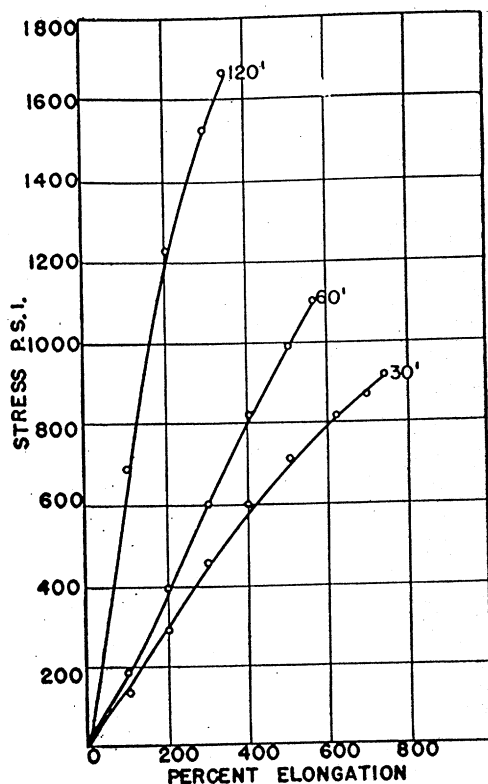


Fig. 4. Stress-Strain Curves of Lactoprene EV Cured with G.M.F. and Triethylene Tetramine (2064)

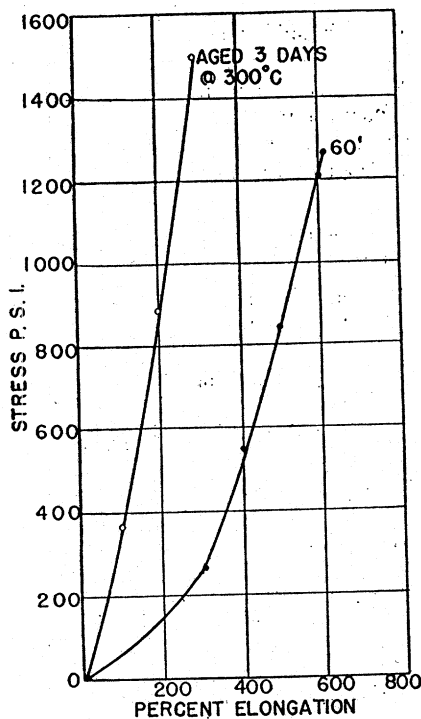


Fig. 5. Stress-Strain Curves of Lactoprene EV Cured with Sulfur, Monex, and Trimene Base (2126)

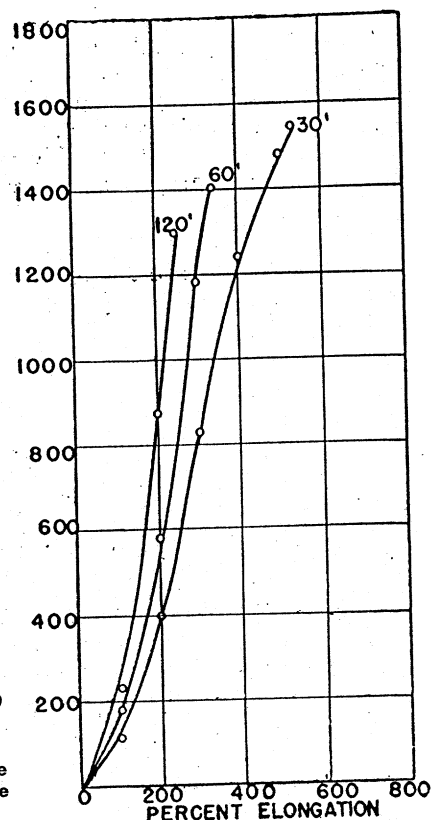


Fig. 6. Stress-Strain Curves of Lactoprene EV Cured with Triethyl Tetramine (2076)

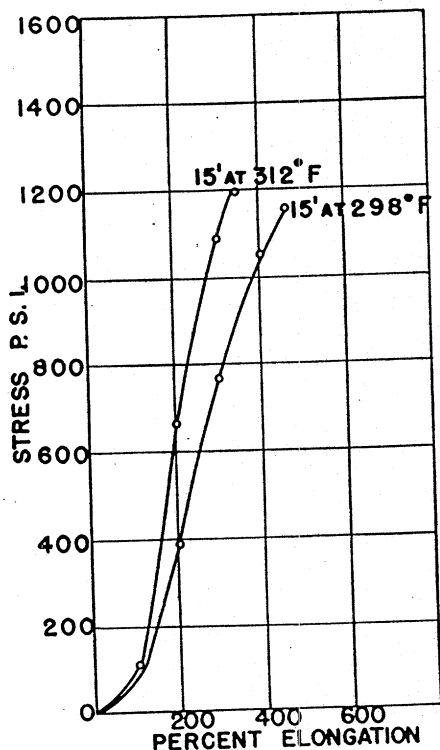


Fig. 7. Stress-Strain Curves of Lactoprene EV Cured with Accelerator 808, Triethylene, and Litharge (2104)

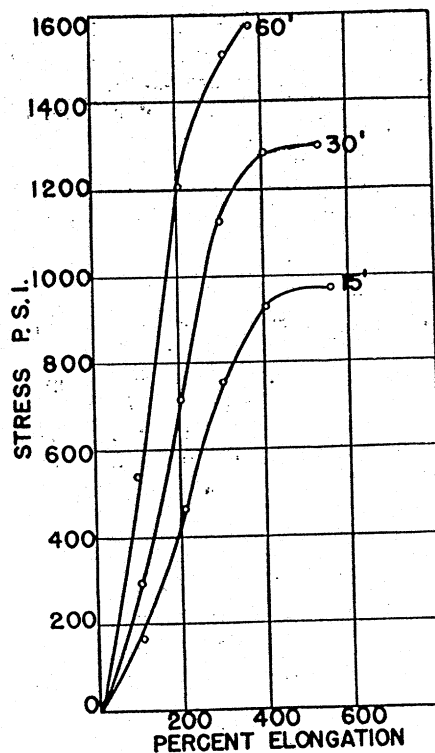


Fig. 8. Stress-Strain Curves of Lactoprene EV Cured with Trimene Base (2113)

These recipes include those based on (a) sulfur and accelerators; (b) Polyac (25), alone or with accelerators; (c) amines and amine condensation products; and (d) agents such as quinone dioxime. Many have been found suitable for curing halogen-containing acrylic elastomers other than Lactoprene EV, such as the copolymer of 95% ethyl acrylate and 5% chloropropyl acrylate. The first three recipes in Table 2 employing (a) sulfur and Monex, (b) sulfur and Pipsolene; and (c) Polyac and Tuads give vulcanizates having good resistance to aging at elevated temperatures. The stress

strain curves of these vulcanizates are given in Figures 1, 2, and 3.

When amines are employed in the vulcanization, a reasonable degree of cure may be obtained in 30 minutes or less at 298° F. as shown in Table 3. A number of the amine recipes are characterized by rapid curing and the production of vulcanizates having low break set, high tear strength, and inverted stress-strain curves as indicated in Figures 4, 5, 6, 7, and 8, respectively.

Data obtained by vulcanizing Lactoprene EV with various sulfur-accelerator and Polyac recipes are given

in Table 1. In general, vulcanization with sulfur occurred at a low rate, and the vulcanizates were heat resistant. The curing rate was improved when sulfur and Accelerator 808 (an amine condensation product) were used together, but probably the improved rate of cure was due primarily to amine rather than sulfur vulcanization.

TABLE 3. VULCANIZATION OF LACTOPRENE EV WITH AMINE RECIPES*

Recipe No.	2081	2092	2088	2105	2112	2113	2086	2080	2085	2102
Accelerator 808 ...	3		5	2				3		10
Litharge	8	5	8	8	4		8		8	
Trimene Base				1	1.5	3	3		3	
Triethylene tetra- mine		1								
Dodecyl dimethyl a- mine										10
SRF carbon black	50	30	50	50	50	50	50	30	50	50
Cure, min., at 298° F.	60	15	60	30	15	15	15	60	120	30
Tensile strength, p.s.i.	1350	1340	1340	1440	1280	1150	1590	1220	1340	1140
Elongation, %	430	720	460	430	530	460	310	600	390	250
Shore A hardness...	60	42	61	52	50	50	60	55	62	56
Crescent tear, lb./in.	236	102	248	183	160	162	127	219	307	95
Resilience, %	2	2	3	2	1	1	2	3	3	3
Break set, %	14	8	16	7	9	11	6	16	17	7
Oven aged 3 days at 300° F.										
Tensile, p.s.i.	2660	1370	2040	2260	1760	2260	2860	2380	2480	2680
Elongation, %	60	90	60	60	60	50	40	90	60	40
Hardness, Shore A	90	75	91	90	84	92	97	90	94	96

* 100 parts Lactoprene EV (Preparation GI57) used in each recipe.

OIL RESISTANCE. To obtain comparative data on oil resistance, lactoprene was compared directly with other oil-resistant rubbers, samples of which were kindly supplied for this purpose by their manufacturers. Natural rubber and GR-S (butadiene-styrene rubber) were not included in the comparative study because these materials are not oil resistant. The samples of different oil-resistant rubbers were immersed into hydrocarbon oils for several days at room temperature, and the extent of swelling was estimated by the convenient method of Garvey (27). Lactoprene EV is more resistant to swelling in certain hydrocarbon oils than the other rubbers except "Thiokol" and Hycar OR. Apparently it is superior to Hycar OR-25 in resistance to some paraffinic oils (3).

Resistance to Heat Aging

The excellent heat aging characteristics of many of the vulcanizates described in Tables 3 and 4 indicate that acrylic elastomers are relatively stable to aging even at elevated temperatures. Probably the heat resistance of acrylic elastomers can be attributed in part to the absence of unsaturation or olefinic linkages in the polymer. Regardless of the explanation, some of the Lactoprene EV vulcanizates are outstanding in heat-aging resistance.

TABLE 4.

AGING OF LACTOPRENE EV AT 300° F. IN MECHANICAL CONVECTION OVEN

Recipe No.	2073*	2147*	2074†	2148‡	2058§
Original:					
Tensile, p.s.i.	1650	1420	1740	1670	1390
Ult. elongation, %	610	620	670	430	710
Shore A hardness	45	39	45	51	38
After aging for 3 days:					
Tensile p.s.i.	1730	1360	1300	1790	1150
Ult. elongation, %	440	430	410	380	610
Shore A hardness	50	44	50	51	37
After aging for 7 days:					
Tensile, p.s.i.	1310	..	970	..
Ult. elongation, %	450	..	500	..
Shore A hardness	45	..	44	..

* Lactoprene EV (100 parts) compounded with sulfur, 2; Monex, 1; and carbon black, 30.

† Compounded with Polyac, 3; Tuads, 2; and carbon black, 30.

‡ Compounded with sulfur, 2; Pipsolene, 1; and carbon black, 30.

§ Compounded with Polyac, 2; Tuads, 1; and carbon black, 30.

Even after being heated in the presence of air at 300° F. for longer than three weeks, some of the lactoprene vulcanizates retain their rubbery characteristics (Tables 2, 3, and 4). As yet the temperature above 300° F. used in the testing of silicone rubber (28) have not been studied with lactoprene.

TABLE 5. COMPOUNDING INGREDIENTS

Ingredient	Composition
Accelerator 808 ...	Tributylidene aniline
GMF	p-Quinone dioxime
Monex	Tetramethyl thiuram monosulfide
Pipsolene	Product of carbon disulfide and methylene dipiperidine
Plasticizer SC ...	Triglycol dioctylate
Polyac	Nitroso compound (polymerized)
Rotax	Mercaptobenzoethiazole
Trimene Base	Triethyltrimethylenetriamine
Tuads	Tetramethyl thiuram disulfide

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